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HYDROPHOBIC ORGANOSILICA COATING ON STEEL AND ALUMINIUM

Mahmood M. H., Suryanto and Sopyan I.
Department of Manufacturing and Material Engineering, IIUM, Malaysia
E-Mail: mahmoodfattah@yahoo.com

ABSTRACT

Superhydrophobic organosilica was fabricated from Tetraorthosilicate (TEOS) as the precursor using a simple sol gel technique and treated by using perfluoroalkysilane. The super hydrophobic silica has been coated on steel and aluminium surface and was characterised based on the silica content on the coating. The results show that the highest contact angle achieved is 108 degree and all the coating has more than 90 degree water contact angle. Since the contact angle is lower than 150 degree, it only managed to get hydrophobic surface instead of superhydrophobic surface. The high contact angle is believed due to presence of air pocket between water and solid surface that enhance by the roughness of the coating. In addition, water contact angle and surface roughness step up with increasing silica content in the coating. The water contact angle of the coating surface can be predicted using the following equation WA=89.39+0.975SR for steel and WA=83.20+1.097SR for aluminium substrates, where WA is water contact angle and SR is surface roughness.

Keyword: superhydrophobic, silica, water contact angle, surface roughness.

INTRODUCTION

Natural super hydrophobicity has recently received much attention and has inspired attempts to create similar surfaces. When water drops on a plant, such as leaf of lotus flower, the water drops can easily roll off of the leaves. This is usually referred to the lotus effect [1]. This effect is related to hydrophobicity phenomenon. The high surface tension on the surface of the lotus leaves causes the water that drop onto the surface of the leaves have a spherical shape and easily removed by rolling droplets. This interesting phenomenon has been noticed quite a long time.

To fabricate material that has the super hydrophobic character, firstly, it must have the appropriate surface morphology that sufficiently rough. This is to allow the formation of the trapped air pocket underneath the water droplets. Secondly, it should have a low surface energy [1]. However, surface roughness of the material is more important property compared to the low surface energy of the material [2].

Many attempted to produce artificial super hydrophobic surface had been successful to copy the natural super hydrophobic surface. The methods include layer by layer film formation [3], electro-spinning [4], carbon nanotube modification [5], photolithographic [6], Chemical Vapor Deposition [7], Chemical etching [8], and self-assembly [9].

There are two important characteristics on the super hydrophobic surfaces: rough surface and low surface energy. Underlying principles to produce the artificial super hydrophobic surfaces can be made by lowering the surface energy of the solid surface and also by make the surface rough at nano or micro scale. However, if only lowering the surface of the solid, it gives a water contact angle of only around 120 degree. To achieve higher water contact angle, proper surface roughness is required. In fact, surfaces with water contact angle more than 150 degree is developed by having proper roughness on materials with low surfaces energy. The contact angle measurement is the way to know the hydrophobicity of the surface [10].

Brassard [11] had made a comparison between the aluminium coated using as-prepared fluorinated silica nanoparticles in the solution and the one coated by diluting the same and both of the samples were coated up to nine layers. The simple sol-gel technique was used in which the silica nanoparticles are synthesized via a Stöber process. In order to obtain low surface energy, these silica nanoparticles are functionalized in the suspension using FAS17 molecules before coating on aluminium substrates. It was then deposited via a spin-coating technique on to the aluminium substrates to obtain super hydrophobic coatings demonstrating large-scale feasibility.

Contact angle is a quantitative measure of the wetting of a solid by a liquid. Thermodynamically it can be thought of as a balance between interfacial energies for the three phases which is solid phase, liquid phase and vapor phase. Thomas Young has created an equation relating this phenomenon and shown in equation 1:

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos \theta_0 \tag{1}$$

Where; γ_{SV} is refer to interfacial energy of the solid-vapor interface, γ_{SL} is refer to interfacial energy of the solid-liquid interface, and γ_{LV} is refer to interfacial energy of the liquid-vapor interface [12]. Figure 1 shows a schematic diagram illustrating a liquid that had been drop to rest on a solid surface. In equation 1 is for the difference

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in chemical nature of the three phases present and assuming the solid surface is microscopically smooth.

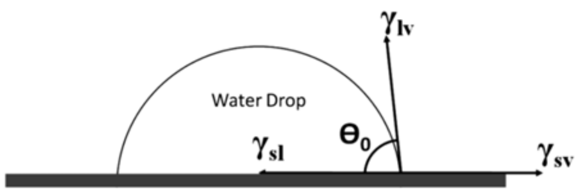

Figure-1. Illustration of contact angle and interfacial energy of a water drop on a solid surface.

For hydrophilic surface, a liquid droplet will spread out and wet the surface and the contact angle of the liquid will be less than 90°. Meanwhile for hydrophobic surface, the contact angle is above than 90°. This phenomenon is occurred because the energy of solid-vapor interface is lower than the energy of solid-liquid interface. This causes the driving force to create a small solid-liquid interfacial area and increases the contact angle to be more than 90°.

There are five types of wetting of the liquid on the solid surfaces that been measured by their contact angle. If the liquid droplet is easily spread out along the surface, the contact angle is 0°, it is a complete wetting. If the contact angle is between 0° to 90°, then it is a hydrophilic wetting and if the angle is from 90° to 150° then it is a hydrophobic type of wetting. Both hydrophilic and hydrophobic types of wetting are the most type of wetting that can be found. Meanwhile if the contact angle is between 150° to 180° then it is consider as super hydrophobic type of wetting. Lastly if the liquid droplet creates a contact angle of 180° then it is considered as complete non-wetting type.

When the liquid is dropped onto a solid surface, it will produce a homogeneous or heterogeneous interface. Homogeneous interface is when the liquid droplet has contact with the solid surface and there is no air-pocket between the solid surface and the liquid. When the liquid is dropped onto solid surface and there are trapped air pockets between the liquid and the solid surface, a heterogeneous interface is formed. The homogeneous interface is developed by Wenzel and is defined by the following equation (2) for the contact angle on rough surface:

$$\cos \Theta_w = r \cos \Theta \qquad (2)$$

Where Θ_w is the apparent contact angle which is corresponds to the stable equilibrium state and r is the surface roughness factor. From the equation, if the contact angle of the liquid droplet on a smooth surface is less than 90º then the contact angle on the rough surface will be smaller. Meanwhile, if the contact angle on a smooth surface is greater than 90º then the contact angle on the rough surface will be larger.

When dealing with heterogeneous surface, the Wenzel model is not sufficient and Cassie and Baxter further extended the Wenzel's equation to include the effect of a heterogeneous interface on contact angles. In this case, the liquid droplet will rest on top of the rough surface and never has direct contact with the solid surface. The air becomes entrapped underneath the liquid droplet. The solid, liquid, and vapor phases contact area can be represented by the fs and fv, which are the area fraction of the solid and vapor on the composite surface. Defining the contact angle in the Cassie-Baxter model is shown in equation (3):

$$\cos \Theta_c = fs (\cos \Theta + 1) - 1 \qquad (3)$$

Based on the above equation, it can be found that if the vapour pocket is removed, the contact angle will be back to the ordinary contact angle.

EXPERIMENTS

Organosilica was prepared by dissolving 2g of Pluronic (P123) into 60ml of hydrochloric acid and stirred for at least one hour. Tetraethyl orthosilicate (TEOS) was added to the solution, stirred for two hours at 40º C and aged at 40º C for 24 hours. After aging process, formed precipitate was filtered, washed and dried. The organosilica was mixed with Perfluorodecyl-triethoxysilane (FAS17) in ethanol solution, dried for about three days to promote stable fluorosilaneted layer on silica surface. The amount of FAS17 diluted onto silica was varied to 0.5 ml, 1.0 ml and 1.5 ml for every 10 grams of organosilica. 2 cm x 2cm polished substrate was coated with organosilica and dried for 3 hours. The coating silica was contained with 10%, 25%, 50% and 75% hydrophobic silica. Two different substrates, aluminium and steel, were used in this investigation.

The particle of organosilica was characterized by using Field Emission Scanning Electron Microscope (FESEM) JEOL, JSM-6700F. The size of particle was measured using SEM and particle size analyser. Contact angle is determine by using Image-J software with drop analysis plugin by analysing the photography taken parallel to the water droplet resting on the substrate surface with Low-bond axisymmetric drop shape analysis. Surface roughness was measured by using Mitutoyo surface test SJ-400 machine while surface topography is studied by using Scanning Electron Microscope (SEM).

RESULTS AND DISCUSSIONS

Figure-2 shows structure and size of coated organosilica. It is shown that the particles size is between 0.4 and 0.8 micrometer. With this size, it is possible to have a surface roughness that may have pocket vapour with water drop or show hydrophobic.

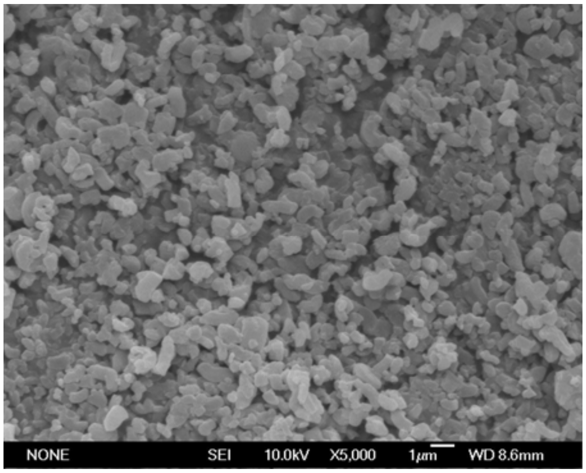

Figure-2. Organosilica coated sample.

Water contact angle measurement was carried out. This is the most important part to determine the surface is superhydrophobic. Firstly the water contact angle testing is done to the sample without organosilica content. This control sample shows that average water contact angle is 59.56 degree which is the hydrophilic type of surface.

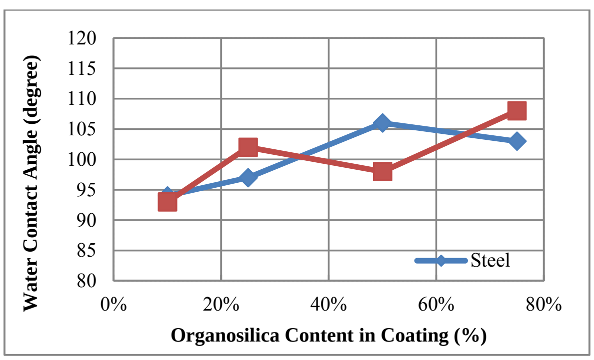

Figure-3. Water contact angle as a function of organosilica content in coating.

Water contact angle of hydrophobic organosilica coating is presented in Figure-3 for both steel and aluminium substrates. It is clearly seen that water contact angle increases with organosilica content in the coating. The increase is linear with slope of 1.2 degree/10% for steel and 1.2 degree/10% for aluminium substrate.

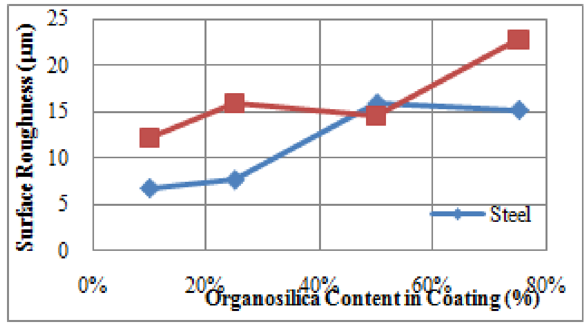

Figure-4. Surface roughness as a function of organosilica content in coating.

Surface roughness of hydrophobic organosilica coating is presented in figure 4 for both steel and aluminium substrates. It is clearly seen that surface roughness increases with organosilica content in the coating. The surface roughness increase is expected to be linear, SR=5.433+15OC for steel and SR=10.833+13.8 SC for aluminium substrates where SR=surface roughness and OC= organosilica content.

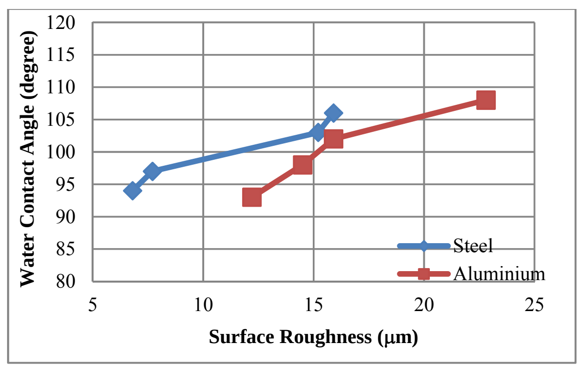

Figure-5. Water contact angle as a function of surface roughness.

Water contact angle of hydrophobic organosilica coating as a function of surface roughness is shown in figure 5 for both steel and aluminium substrates. It is clearly seen that water contact angle increases with surface roughness of coating. The water contact angle of the coating surface can be predicted using the following equation WA=89.39+0.975SR for steel with R^2 = 0.935 and WA=83.20+1.097SR for aluminium substrates with R^2 = 0.938 where WA = water contact angle while SR=surface roughness.

CONCLUSIONS

Hydrophobic silica had been successfully fabricated using sol-gel method using TEOS as a precursor to make the organosilica which then treated with perfluoroalkysilane. The water contact angle testing,

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surface roughness measurement and surface topography characterization had been studied. The highest water contact angle been achieved by the coating is 108 degree and all the water contact angle is above 90 degree. Since the contact angle is lower than 150 degree, it only managed to get hydrophobic surface instead of superhydrophobic surface. Water contact angle is found to be affected by surface roughness. The water contact angle of the coating surface can be predicted using the following equation WA=89.39+0.975SR for steel and WA=83.20+1.097SR for aluminium substrates.

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